

## Study of Formation of Co and Zn Phosphates in Solvothermal Synthesis using Piperazine and 2-methylpiperazine as Templating Molecules

A. Christensen, R. Nielsen (U. Aarhus), P. Norby (U. Oslo) and J. Hanson (BNL, Chemistry)

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The compounds  $[\text{Zn}_2(\text{PO}_4)(\text{H}_{1.5}\text{PO}_4)_2]\text{C}_4\text{H}_8\text{N}_2\text{H}_4$ ,  $[(\text{Co}_{0.44}\text{Zn}_{0.56})_2(\text{PO}_4)(\text{H}_{1.5}\text{PO}_4)_2]\text{C}_4\text{H}_8\text{N}_2\text{H}_4$ ,  $[\text{Zn}(\text{HPO}_4)_2]\text{C}_5\text{N}_2\text{H}_{14}$  and  $[(\text{Co}_{0.25}\text{Zn}_{0.75})(\text{HPO}_4)_2]\text{C}_5\text{N}_2\text{H}_{14}$  were obtained in solvothermal synthesis using piperazine or 2-methylpiperazine as templating molecules. Syntheses were made in teflon lined pressure vessels at temperatures up to 190°C and the crystallization processes were investigated by real time *in-situ* measurements of synchrotron X-ray powder diffraction patterns at temperatures up to 200°C.

The *in-situ* synchrotron X-ray powder diffraction investigation of the reaction mixtures was made on a MAR-diffractometer at the beam line X7B at NSLS, Brookhaven National Laboratory. The reaction mixtures were kept in 0.7 mm diameter quartz glass capillaries at an internal pressure of up to 25 atm, and the capillaries were heated with hot air for a temperature ramp from 25 to 200°C. The temperature of the hot air flow was monitored with a chromel-alumel thermocouple and calibration of the temperature of the capillary was made from measurements of the thermal expansion of a sample of a silver powder and from measurements of the melting point of sulfur housed in a capillary. The wavelength used was 0.9378 Å and Bragg reflections out to  $\sin\theta/\lambda = 0.22 \text{ Å}^{-1}$  could be recorded. The MAR-diffractometer recorded a diffraction frame in 82 sec, and the temperature ramp was set to go from 25 to 200°C in 120 min, yielding 88 frames for this temperature range corresponding to  $\Delta T = 2^\circ\text{C}$  per frame. The frames were integrated using the software FIT2D and the powder patterns were displayed as a stack of patterns showing Bragg reflections occurring or disappearing during the experiment. The crystalline reaction products were identified from their X-ray diffraction powder patterns.

**Zinc-2-methylpiperazine-phosphate:** The reaction mixture had the following molar ratios: 2-methylpiperazine 0.92: ZnO 0.31:  $\text{P}_2\text{O}_5$  1.00: ethylene glycol 11.2:  $\text{H}_2\text{O}$  38.5. The heating ramp was from 25 to 200°C and the stack of powder patterns is displayed in the figure. The reaction mixture is crystalline at the start of the experiment and the Bragg reflections increase in intensity during the heating corresponding to additional crystallization of amorphous material. The reaction product is identified from the powder patterns as a pure sample of  $[\text{Zn}(\text{HPO}_4)_2]\text{C}_5\text{N}_2\text{H}_{14}$ .

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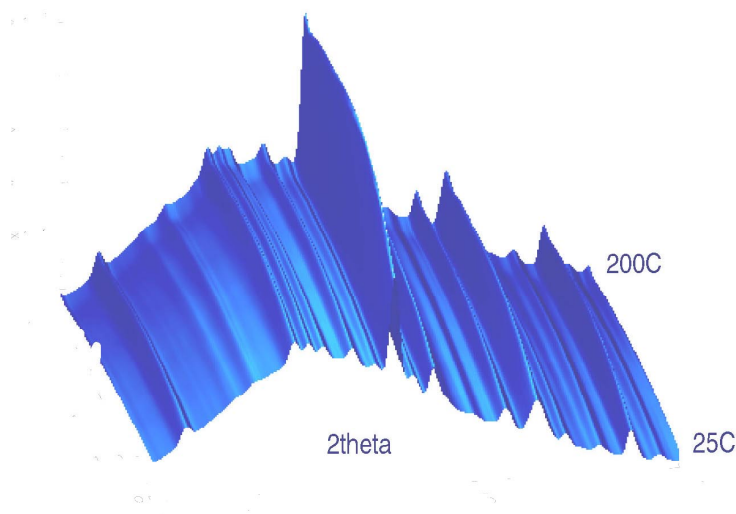


Figure 1. Ramp temperature from 25°C to 200°C.